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Liquefied Petroleum Gas (LPG) as a Fuel for Internal Combustion Engines

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Additional information is available at the end of the chapter

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Abstract

Liquefied hydrocarbon gases, containing mostly the mixture of C3-C4 hydrocarbons, in many countries serve as an important source of energy, also for internal combustion engines. On a world scale, at present, about 270 million tonnes of this fuel is produced, of which motorization consumes 26 million tonnes (~10%). Poland is one of these countries, where LPG is a popular engine fuel. Annual consumption of so called autogas is about 1.7 million tonnes with increasing tendency. Almost 3 millions of cars with bifuel engines, mostly spark ignition ones, are driven on Polish roads. An extensive logistical infrastructure accompanies the development of the use of this type of fuel in Poland. There are numerous production companies in Poland working to meet the needs of this branch of industry, as well as a modern service base. Intensive research and development works in this field are carried out. The exceptional advantages of LPG as an alternative engine fuel have been highly appreciated in Poland. These advantages result mainly from the simplicity of its production. Relatively low investment costs and energy consumption are needed to produce high-quality fuel by degasolining of natural gas or crude oil stabilization. LPG is produced as a byproduct in numerous petroleum refining processes and its quality is relatively close to the engine fuel requirements. The source of aliphatic hydrocarbons falling into LPG range can also be the processes of biomass conversion and in the near future, fermentation processes. Environmental advantages of LPG are primarily very low emission of almost all toxic components of engine exhaust gases compared to gasoline or diesel fuel. In this chapter the results of research works aimed at the improvement of exploitation properties, logistics and LPG combustion processes in spark ignition engines are presented. In this area, anti-corrosion additives for LPG of very high effectiveness were obtained and tested. Also, with the help of additives, the problem of water separating from LPG during storage and transport in tankers has been solved. A multifunctional additive was obtained giving LPG adequate lubricity and detergent properties. The influence of water on the process of LPG combustion in a gasoline fuelled engine as well as ways to supply water to the combustion zone are being studied. A mathematical model is being elaborated, precisely describing correlations between density and chemical composition of LPG as well as changes of density as a function of fuel tempera-

ture. In the realization of these plans LPG producing companies, research and development teams as well as producers of automobile LPG systems are involved. Successful completion of research works and design works will result in elimination of scarce disadvantages of LPG as an engine fuel, preserving at the same time all its numerous advantages as an alternative fuel for the future - the new era source of energy.

Keywords: Liquefied petroleum gases (LPG), corrosion, , water, additives, combustion, density modeling

1. Introduction

The mixture of liquefied hydrocarbon gases C_3 - C_4 (propane and butane), called colloquially liquefied gas or LPG, is a particular energy carrier, counted among the group of alternative fuels. LPG has more than 1000 different uses, including applications in industry, civil engineering, communal economy, agriculture, households, and transport. Because of simplified logistics of transport ensuring supply diversification, availability of sources, and most of all environmental aspects, LPG exhibits high dynamics of production and consumption; the global production of this fuel comes close to 280 million tonnes.

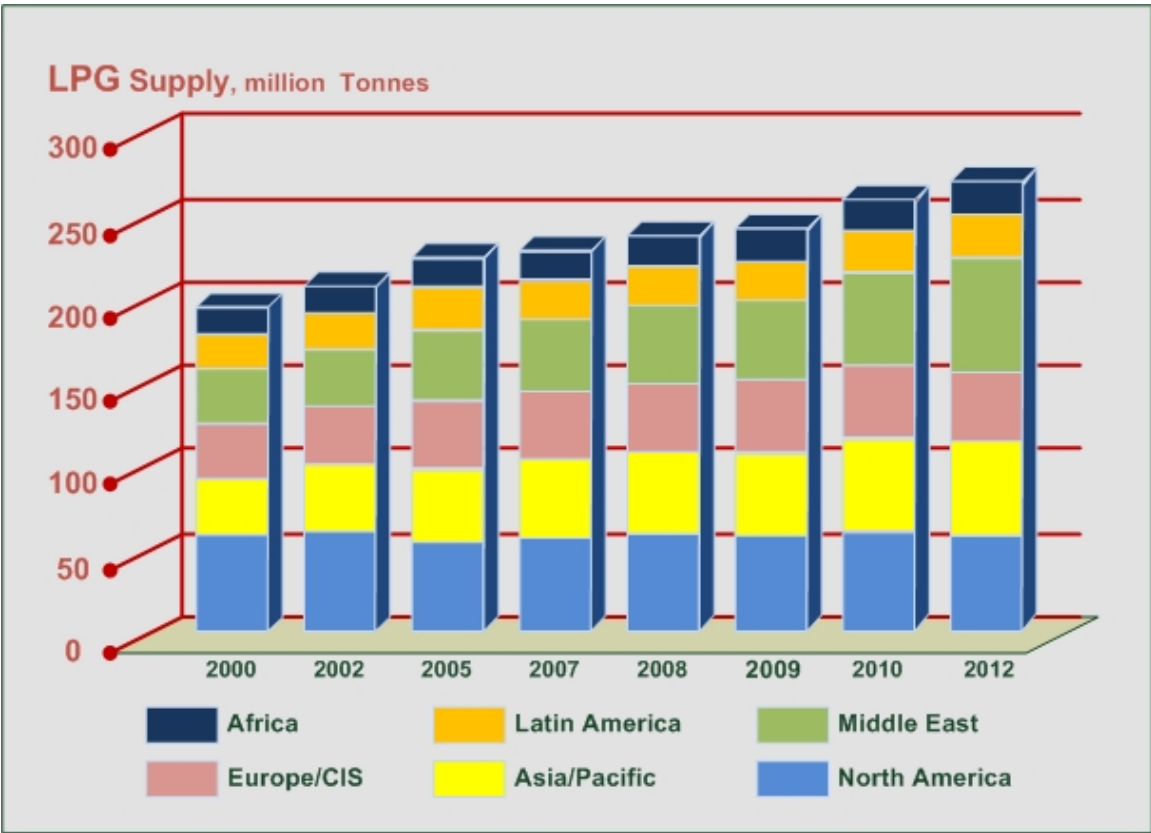


Figure 1. Global consumption of LPG [1]

Only a small part of global LPG production, about 10%, is used to fuel internal combustion engines.

Liquefied gas is produced from three main sources:

- As a byproduct from degasolining of natural gas,
- As a byproduct from stabilization of petroleum in crude oil mining site,
- As a byproduct from petroleum refining in a refinery.

Natural gas contains mainly methane, but also other substances, among them heavier hydrocarbons, including C₃ and C₄. Such gas is called “wet” and its preparation for transport requires the removal of LPG fraction – degasolining. Additional amounts of LPG are obtained during stabilization of crude oil at a mining site, being a part of petroleum preparation for the transport. It is estimated that globally about 60% of LPG is obtained that way [2]. Purified “liquid gas” contains mainly propane, butane, and isobutane in different proportions, but it does not contain unsaturated hydrocarbons. This makes it a fuel of highest quality and best chemical stability.

The other 40% of LPG is obtained during petroleum refining in a refinery. Depending on the kind of crude oil, it contains 1–4% of LPG fraction. The source of saturated hydrocarbons, being components of liquefied gas in a refinery, is distillation operations and numerous types of hydrotreating. Most fractions obtained from distillation of high-sulfur feedstock are hydro-treated. The wide spread of hydrotreating processes in the manufacturing of refinery products was caused by strict environmental regulations. In this way the feedstocks for the isomerization of light gasoline fractions and catalytic reforming of gasolines are prepared. Hydrodesulphurization of catalytic cracking feedstock is being introduced to refinery schemes. Hydrotreating is used to purify the components of jet fuel, diesel fuel, light heating oil, base lubricating oils and petroleum waxes. Deep petroleum refining means also the use of destructive hydrogen processes, hydrocracking of vacuum distillates and residua. As an effect of reduction with hydrogen of sulfur, nitrogen, and oxygen compounds, hydrocarbons are formed, including C₃–C₄ – Figure 2.

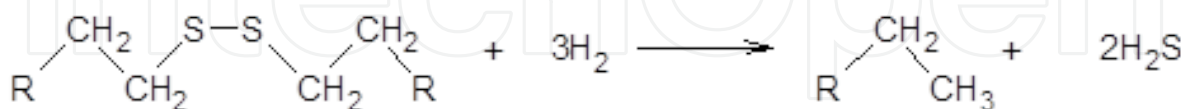


Figure 2. An example of hydrogenation of alkyl disulfide

LPG fractions obtained from thermal destructive processes, such as cracking or pyrolysis have slightly different chemical nature. They contain olefins and dienes, valuable chemicals, which can be found in LPG fractions used as motor and heating fuels.

Summarizing, it can be said that LPG is obtained as a byproduct from petroleum and natural gas refining, which causes that it must be a cheap product. Its improvement for the use as a

motor fuel requires most often the reduction of sulfur content to the level required by environmental regulations.

The technology of autogas production can be much more complicated in situations when a fuel of normalized quality has to be produced from various components of varying chemical composition. Additional technological and logistical complication in autogas production can be a variation in properties of this fuel depending on the season of the year and climatic conditions.

The quality requirements for LPG in Poland are the same as in the EN 589+A1:2012 standard. The only differences are related to, so called, winter parameters, which each country defines adequately to its climatic conditions. LPG in Poland, since 2007, is subject to the same national fuel monitoring and control system, as other fuels, that is, gasolines and diesel fuels. The regulation governing this system is one of the most strict in Europe. The quality monitoring of motor fuels is supervised by the Office of Competition and Consumer Protection (UOKiK) and is carried out at each stage of logistical chain, starting from the producer, through shipment, storage, transport, and finally fuel stations. For many years, the results of LPG sample analyses have been very good. In 2014, only 1.5% of the LPG samples collected at fuel stations did not fully fulfill the normative requirements for these fuels. No deviations from required properties were found for samples collected from the tanks belonging to the producers and wholesalers. Only great effort undertaken by the autogas industry in the area of optimization of procedures and high investment in quality control systems led to obtaining such results.

What is characteristic for LPG quality requirements is that they do not contain its hydrocarbon composition. On the other hand, the producers cannot use any mixtures they choose, because the need to use particular chemical compositions is caused by the requirements for other key properties influencing the engine operation. These parameters include:

- Motor octane number
- Relative vapor pressure at 40°C
- Temperature at which the vapor pressure is not lower than 150kPa

The adequate value of motor octane number (≥ 89) of a fuel is required for correct and economical combustion in an engine. Indirectly, the standard ensures that LPG as a motor fuel has a research octane number, used to characterize gasolines, on a level higher than 95, often above 100.

It has to be noted that autogas evaporates in 100% in a cylinder, which cannot be said about gasolines and particularly about diesel fuels. Full evaporation is a factor deciding that LPG, despite having potentially lower calorific value than gasoline, does not have to be consumed in higher quantities.

Easily available sources of autogas components, increasing production of natural gas from unconventional sources, accompanied by C₃-C₄ hydrocarbons as well as reports relating to production of propane from biomass conversion indicate that this fuel has good perspectives for the increase of supply and further spread of its use.

LPG is an exceptional fuel, which is indicated by not only its availability but also by production costs. The comparison of costs or energy needed to produce modern gasolines or diesel fuels indicates that the production of LPG is much cheaper [3, 4].

LPG is rightly treated as an environment friendly fuel, not only because of production costs, but also because of social and ecological profits. A very dangerous and socially costly component of gases emitted from internal combustion engines is particulate matter (PM). The comparison of health costs of motorization is presented in Table 1 [5].

Component of exhaust gases	Health costs, EUR/t
PM _{2,5}	160.000
SO ₂	10.000
NO ₂	15.700
VOC	700
CO	20

Table 1. Evaluation of health costs related to the emission of components of exhaust gases

Engines fueled with autogas emit incomparably lower amounts of these components, which causes that total social costs of using different motor fuels are lowest for LPG – Fig. 3.

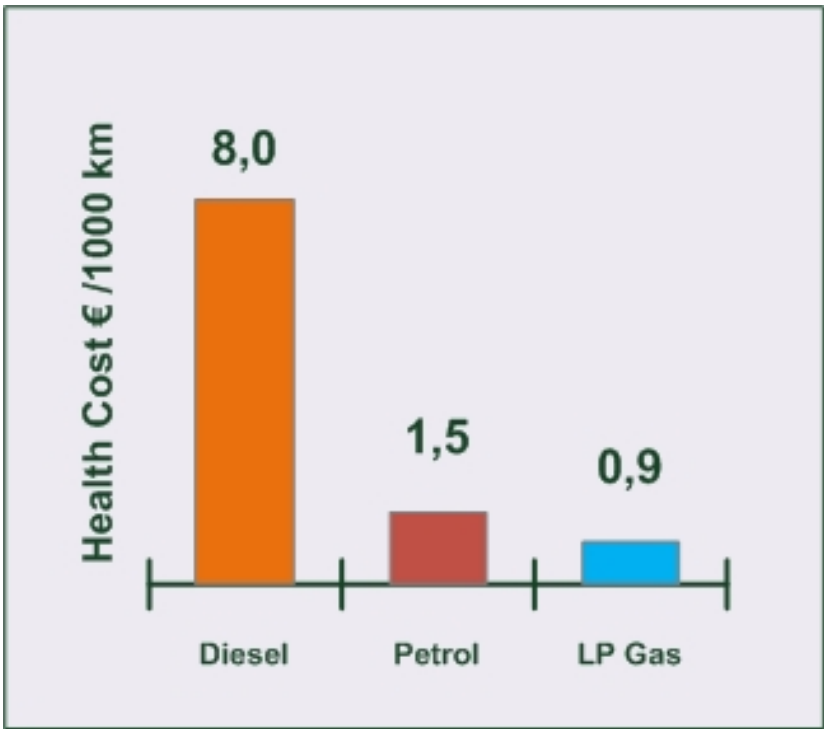


Figure 3. Health costs of using different motor fuels

Higher calorific value of autogas, compared to gasoline and diesel fuel, along with higher hydrogen to carbon ratio, leads to emission of lower amounts of carbon dioxide (73.6 g CO₂/MJ while for gasoline it is 85.8 CO₂/MJ, and for diesel fuel - 87.4 g CO₂/MJ).

The use of LPG as an alternative motor fuel needs relatively small and not expensive adaptations in spark-ignited engines. Automobile producers play a bigger and bigger role in the popularization of autogas. They noticed the economical and ecological profits from the use of such engines and more often offer automobiles with factory installed autogas systems. It creates a positive image of autogas as a fuel environmentally friendly, economical, and fully safe.

2. Autogas in Poland

For the energy policy, in the conditions of sustainable development, total costs of motor fuels, well-to-wheel, are very important, if the number of vehicles with internal combustion engines and the amount of fuel consumed by them are taken into account. Poland, in this aspect, is in a very good situation because of a vast number of bi-fuel vehicles and high participation of autogas in motor fuel consumption. More and more common treating of LPG as an alternative fuel is profitable for its wider use, both in transport and in other areas.

The beginnings of autogas industry in Poland reach the last decade of the twentieth century, when first legal LPG automobile installations appeared. Intensive development of this sector of the economy occurred at the turn of the century. The amount of autogas sold in 1996 was 250000 tons, in 2003 it was more than 1 million tonnes, and in recent years it got stabilized at the level of 1.5–1.65 million tonnes.

In Poland, the number of vehicles equipped with LPG installations constantly increases. After more than 20 years of autogas history in Poland, it is currently more than 2.85 million. It means that almost one in seven cars on Polish roads is fueled with LPG. It is estimated that globally the number of such cars is higher than 25 million, and Poland, along with South Korea, Turkey, Italy, and Australia, is a country with the highest population of bi-fuel cars (gasoline-LPG).

This fuel is easily available in Poland, because the number of autogas stations has reached 5500 and since 1998 it increased three-fold. Since a few years the increase of network stations offering autogas can be noticed. Novelization of regulations, allowing unassisted autogas fueling, fosters this process.

Many firms and companies import and distribute LPG in Poland, having well developed infrastructure, means of transport, and most of all qualified personnel. A fragmented structure of the import favors competition on the market and full elasticity in choosing the direction from which the liquefied gas is imported.

Polish LPG market in 2013 (2200000 tonnes) is composed of 17.7% of local production (Orlen Gaz, Lotos Paliwa, PGNiG) and imports from the Russian Federation (over 50%), Kazakhstan (over 25.1%), and Belarus (11.8%). Poland also exports LPG [6]. The structure of the LPG market

has not been changed for years. The main role is played by autogas (almost 75% of the market). The second place is taken by 11 kg tanks (over 13%), used in 5.4 million households. About 12% of the market encompasses the segment of industrial and household LPG storage tanks.

During the last 20 years numerous companies were formed, producing LPG for the needs of local market and developing export to countries located on all continents. Basing on incomplete data, it can be estimated that 13 local producers of automobile LPG systems produce annually about 2 million such installations. These companies employ from several dozens to about 500 employers each. The characteristic feature of these companies is usually a wide profile of production, designing new elements of these installations and control systems. It is connected to having their own design and technology supply base, and some of these companies have research and development centers, cooperating with scientific and research institutes.

An example of such a company can be AC SA from Bialystok, noted on the GPW stock exchange. It is a leading company in Poland and a notable global producer of automobile LPG/CNG systems marked STAG. On the Polish automobile market, AC SA is present for 27 years, employs over 500 people and at present it is the largest company operating in the area of automobile gas installations in the country. As the company's evaluations indicate, it has over 50% share in the Polish market. The AC SA products reach over 40 countries all over the world. In 2011, the export made 63% of the AC SA total revenue. The key foreign recipients of AC SA include Germany, Russia, Ukraine, Turkey, and Thailand [7].

Qualified personnel, modern machinery park, efficient management, and marketing allow the expansion on foreign markets, including contracts with automobile producers for the delivery of "factory installed" LPG installations for new vehicles.

The development of the industry and increasing quality requirements of the customers, as well as the development of new engine technologies, initiated the process of formation of networks of garages authorized by the producers, with monitored service quality, elongation and widening of warranty range for offered LPG systems.

High safety and quality level of installations produced in Poland is an effect of very strong internal and foreign competition as well as fully functioning this branch in open market conditions.

The presence of foreign companies, mainly Dutch and Italian, representing highest global level, increases the competition and favors the technological development of Polish producers.

Over 20 local companies and a few foreign ones produce parts for the producers and service of LPG installations. Among them are both small and young companies as well as medium and big firms with long tradition. Five companies produce LPG tanks, adjusted to the varied needs of recipients. Over 1 thousand types and models of LPG tanks are produced. Local makers produce their own reducer-evaporators of liquefied autogas, injectors, pressure hoses, plastic elements, gas, and liquid phase filters. All producers are also exporters, cooperating with customers on all continents. One of the producers opened his representative office on very quickly developing the US market. The predominant directions of export for local producers are Eastern European countries as well as "old European Union", South America and Far East.

The dynamically developing LPG market in Poland induced the creation of companies designing and realizing investments in the area of construction of fueling stations, terminals, and fuel bases. These companies include design groups, firms installing and servicing IT systems for LPG industry, as well as telemetry systems, companies legalizing equipment and tanks. In total there are at least 10 companies of various size in this area.

In Poland there are about 1550 active companies installing and servicing automobile LPG systems [8]. Most of these workshops have the authorization of a given installation producer, maintaining contacts and training meetings with installation makers. Well-trained installers often help the customers to choose optimal solutions, passing their remarks and notifications to the producers. In this way they are cooperating in the creation of new solutions and improvement of technologies.

The innovative character of the LPG industry is realized as a natural need to remain on local market as well as to expand its actions abroad.

High popularity to use LPG as a fuel for spark-ignited engines caused that it started to be used in diesel engines. Diesel gas systems for engines fueled with diesel fuel and LPG give fuel consumption reductions from 10% to 20%. More efficient combustion of diesel fuel increases the engine power, reduces the emission of carbon (II) oxide and particulate matter, while it does not reduce the lifetime of an engine.

3. Quality issues of LPG as a motor fuel

Autogas, having many advantages, exhibits also several disadvantages compared with modern gasolines. The standard requirements do not allow to introduce additives to LPG, which in gasolines provide many key properties, such as cleaning of fuel supply system, reducing the need for octane requirement increase (ORI), thermal and thermo-oxidative stability, as well as anti-corrosion properties.

The aim of the research works described in this chapter is:

- Improvement of the quality of LPG in terms of corrosive activity against copper
- Increase of the accuracy of LPG analysis, in particular the determination of total sulfur content and corrosion against copper, through a new way of LPG sampling for analysis
- Improvement of LPG logistics taking into account the water content in the fuel as well as the influence of the chemical composition and temperature of the fuel on its density
- Improvement of LPG combustion process in an engine by introducing water into the combustion zone

3.1. Corrosion

One of the most important quality parameters of autogas is lack of corrosion activity against copper. In practice, however, the situation can happen that the corrosivity of this fuel appears

in the logistics chain. Good quality LPG shipped via railway tankers and/or stored in tanks can dissolve chemical compounds that can cause the corrosion of copper plates. There is much evidence that the cause of this corrosion threat is water which stays at the bottom of tanks and contains various micro-contaminations. These substances in water undergo i.a. hydrolysis reactions, generating corrosive compounds, such as hydrogen sulfide.

In analytical practice, there are controversies related to the corrosivity of LPG. Using high quality instruments does not guarantee the repeatability of results. It appears that exceptional attention should be paid to the procedures of fuel sample collections.

3.2. Collection of LPG samples

Collection and transfer of representative sample of a material has key influence on the evaluation of its quality parameters. Proper collection of a representative sample has particular importance because of the increase of quality requirements for LPG, development of analytical techniques, and higher experience of the laboratory personnel. Often the operation of collection and preparation of the sample is the most neuralgic point, influencing the correctness of quality parameter evaluation for this batch of a product.

The issue of proper transfer of analytical sample from a product batch was undertaken during comparative studies organized by the Automotive Industry Institute (PIMOT) in 2013 [9]. These studies were carried out in almost ideal conditions, where all participants were prepared for the collection of samples, preparing all equipment according to every procedure in order to obtain maximum purity of the samples. The cleanliness of the sample collection equipment and the ability to maintain it in daily use, using present solutions and with high frequency of sample collection is very hard to achieve. As practice shows, often for random comparative studies on samples, collected during everyday operations, some of the results differ significantly, particularly for parameters such as total sulfur content and corrosivity against copper. It can be related to the difficulty with maintaining high cleanliness of the equipment.

The differences in the assessment of obtained results are often the subject of disputes between LPG importers and producers and controlling authorities, monitoring the quality parameters included in standards for LPG fuel. Presently used solutions and their effects in the form of differences in analytical results of the same LPG fuel are often cause for fines for the companies taking part in LPG trade. The authority verifying the quality is the State Trade Inspection (PIH), exerting regulations in the name of the Office of Competition and Consumer Protection (UOKiK) and Energy Regulatory Office, and in the case of finding that the fuel does not fulfill quality standards, it imposes fines.

In Poland, an innovative solution was used, enabling precise evaluation of the quality and classification of fuels, not only protecting final recipients but also the interests of individual entrepreneurs, at the same time stimulating the further development of this industry.

Available literature does not discuss this issue in the aspect of possible analytical problems, except for the current PN-EN ISO 4257 standard, related to the collection of LPG samples. Taking into account the development of the technology and problems that are met in LPG analytics, a solution has been elaborated which can eliminate this problem. This solution allows

collection and transfer of a representative sample from product batch and then its proper evaluation [10].

New technical solution, related to the demountable sampler of specially prepared internal surface, has been subject of profound comparative studies. In these studies, the results of LPG quality parameter measurements using two different types of samplers and ways of cleaning them were compared. During these studies, the influence of sampler design and the way of its preparation for sample collection as well as its cleanliness on the representativeness of quality assessment was evaluated. Studies were carried out in the area of the evaluation of the quality of collected LPG samples and microscopic scanning of internal surfaces of the samplers.

Non-damaging and damaging tests on the samplers of two different designs were carried out in order to obtain information on the influence of sampler design and its internal surface on the processes occurring in the sampler and the representativeness of the sample. Standard non-demountable sampler, made of chromium-nickel 316L steel, was compared to a demountable sampler made from chromium-nickel 316Ti steel. Additionally, in a new demountable sampler, the internal surface was prepared by mechanical polishing, finished with etching and chemical electropolishing. The surface prepared this way was passivated with oxides. Figure 4 presents the two types of samplers, along with their cross-sections.

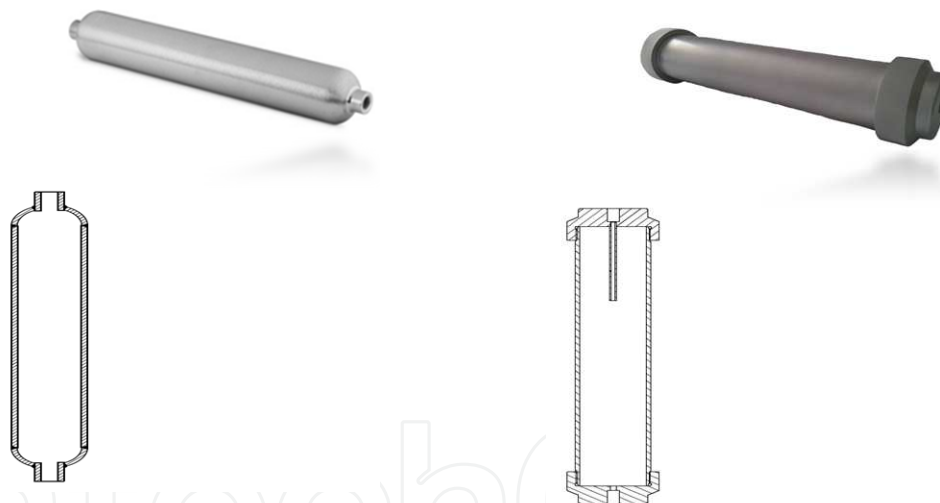


Figure 4. Traditional, non-demountable sampler [left], demountable sampler [right]

In the case of a demountable sampler, as a new solution, using the processes of etching and chemical electropolishing was aimed at the decrease of surface microporosity, which reduces the threat of aggregation of deposits and chemicals on the surface and makes it easier to clean. Operation applied for the preparation of the internal surface of the sampler uncover homogeneous, clean metal surface, close the micropores, precluding chemical contaminations to adhere to the surface. Electropolishing facilitates further passivation of the surface. The role of the passive surface is protection from adhering chemical compounds to the internal surface of the sample, which can accumulate and influence the correctness of results obtained during long term use of the sample.

Non-damaging, microscopic scans of an internal surface of the sampler showed the surface structure in both types of solutions. The surface of a non-demountable sampler (Figure 5), in places where no additional finishing was used, is very uneven, has noticeable scratches, and sharp edges. On such surfaces, contamination can very easily adsorb and accumulate, having influence on the results of LPG analysis collected with this sampler. High surface roughness makes it hard to clean, which causes the possibility that secondary reactions in the cylinder can occur and the quality parameters of collected samples can change. In the case of a demountable sampler (Figure 6), where additional finishing was applied to the internal surface, it is smooth, the pores of the material are closed, and the structure is homogeneous. Surface prepared in this way impedes the deposits and contaminations to adhere and accumulate on it, increasing the representativeness of collected samples. Lack of possibility to accumulate contaminations simplifies cleaning, which is more efficient. Thus, the sampler is cleaner and provides better representativeness of obtained analytical results.

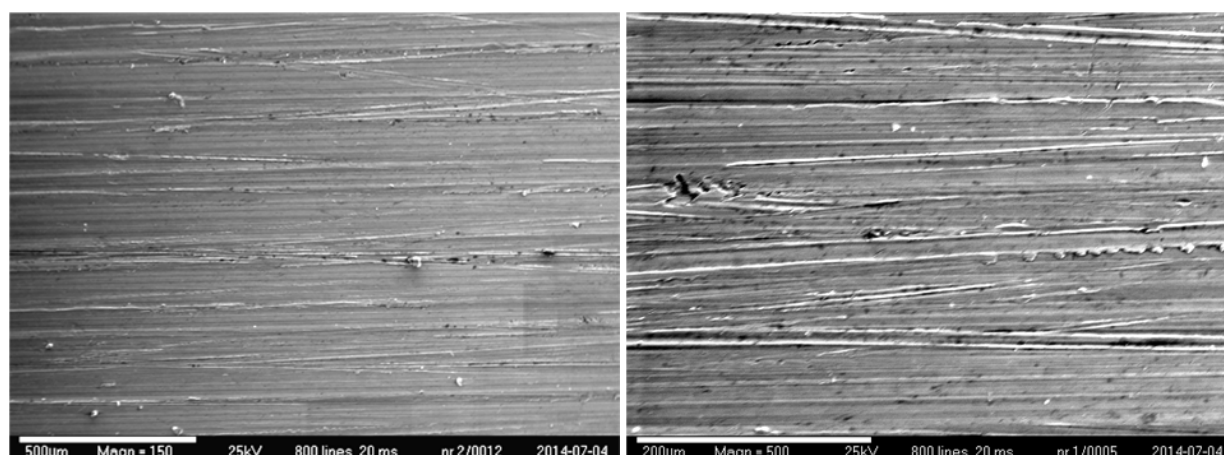


Figure 5. Internal surface of a non-demountable sampler (150x magnification [left], 500x magnification [right])

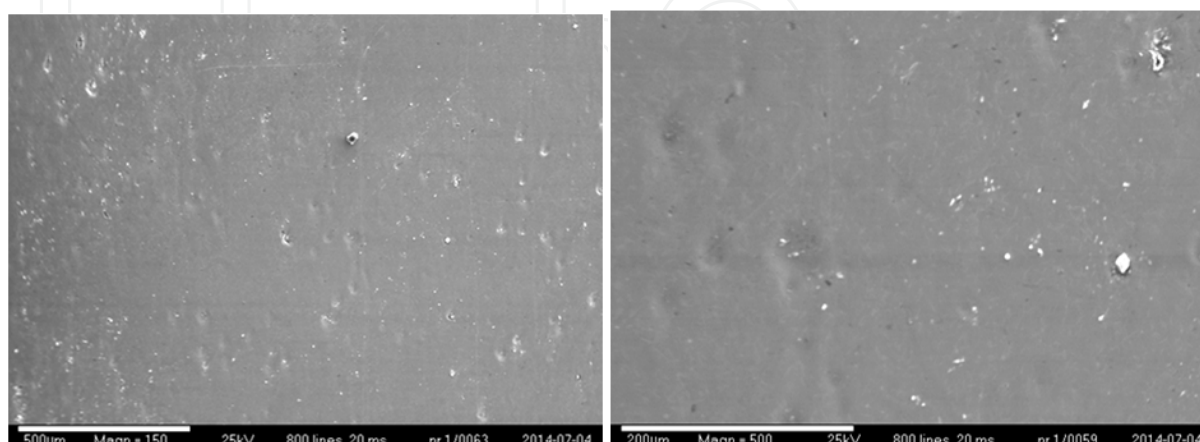


Figure 6. Internal surface of a demountable sampler (150x magnification [left], 500x magnification [right])

Also destructive tests have been carried out that demonstrated the differences in both types of samplers. Each sampler was used to collect 250 samples of LPG. Samplers were cleaned, according to the PN ISO 4257 standard, before each collection. After a series of tests, both samplers were cut along their axis in order to analyze the internal surface of a cylinder. In the case of a new, demountable sampler, no contamination was observed. In the traditional, non-demountable sampler, a dark deposit was observed on its internal surface. Analysis of the deposit indicated the presence of such elements as Na, K, Mg, Ca, Al, V, Ni, Co, Mn, Fe, and S. The most undesirable element in this group is sulfur. The analyzed deposit contained 0.72% m/m of this element. Sulfur in the deposit occurs mainly in the form of inorganic compounds, which in favorable conditions can undergo secondary reactions, forming hydrogen sulfide and sulfur.

Samples collected using both types of samplers under identical conditions were analyzed qualitatively in the same way. In different periods of time, during 3 years, 2113 analyses were made according to the standard procedures. For the parameters such as corrosive activity against copper and total sulfur content, the deviations of the results for some samples had decisive importance for proper qualitative classification of the fuel. Some analytical results for samples collected with a traditional sampler indicated qualitative inconformity of tested fuel with the requirements of the regulations. Biggest deviations were noted for the parameter “corrosive action against copper” – about 8% deviation of the results – and for “total sulfur content,” where the differences quantifiability reached 11%. It has to be noted that the increase in discrepancy of obtained results with the time of use of samplers was observed. This fact can confirm the thesis that secondary reactions occur, having direct influence on the analytical result and consequently on the representativeness of the samples.

The results of comparative studies in operation of the two types of LPG samplers, a traditional one and a newly designed construction, indicate that the new solution has significant advantages, particularly for the objective assessment of LPG quality in the area of total sulfur content and corrosive action against copper. These parameters are at the same time the most frequent causes of exceeding the LPG quality standards.

The value of the new solution is confirmed by awarding it a patent [11] and registering it as an European registered design.

This technical solution and studies on its application was twice distinguished and awarded in the “Naped Nowej Ery” (New Era Drive) competition. It has been used since 2010 with very good results, not only for collecting LPG samples but also for analyses of other technical gases of very high purity.

Strict qualitative requirements and the specifics of LPG transport and storage require in some situations the use of particular additives, in order to fulfill standard parameters or for efficient and safe logistics.

3.3. Anti-corrosion additive

In Poland the problem of LPG corrosivity was solved a few years ago by elaboration and introduction of an anti-corrosion additive of a very high effectiveness [12]. The application of

this additive in an LPG exhibiting the corrosivity level higher than 1, up to 4, causes reduction of the corrosivity class to level 1a. The additive contains a composition of slightly basic nitrogen compounds in high concentration in an appropriate mixture of solvents which provide good miscibility of active substances with liquefied C₃-C₄ hydrocarbons, practically in all temperatures. Nitric bases have the ability to neutralize acidic, corrosive components of LPG, hydrogen sulfide, and mercaptans. In turn, the affinity to metals of surfactants, contained in the additive, causes the creation of an adsorptive layer on the surfaces of copper and also steel. This layer forms a protective barrier and also improves the lubricity of the fuel containing the additive. The lubricity action of the additive, confirmed in High Frequency Reciprocating Rig (HFRR) tests, causes the reduction of average friction coefficient from 0.591 to 0.257, and 10-fold reduction of wear (by 89.3%). A significant advantage of this product has to be underlined – it is mixed with LPG in a 1:8000 (v/v) ratio and practically it does not increase a standard parameter residue after evaporation (oil residue). Experiences collected during several years of use of this additive by Polish LPG producers and importers, as well as observations made by foreign customers, confirm the high efficiency of the additive.

4. Water in the fuel

LPG exhibits very limited solubility of water but despite this, technological operations carried out at increased temperatures and then cooling during transport or storage cause the separation of water. As a result, at the bottom of tanks and railway tankers, almost always there is a layer of water. The unloading of LPG, particularly during autumn or winter, causes in such situations the blockage of unloading valves with ice. This situation is particularly difficult for automobile tankers supplying autogas fueling stations. Similar problems can occur in the distributors of LPG while fueling cars with water-contaminated fuel. The practice of LPG logistics, as well as European standards, recommend in such situations adding to the tanks and tankers small amounts of methanol. It is an accepted solution, but having some disadvantages. Methanol mixes with water in all proportions, lowering its freezing point, but it does not mix with the fuel. In this way, the volume of water phase in the tank increases, which can cause its increased transfer to further volumes in the logistical chain. The original solution used in Poland is based on the addition of a special additive to the water-contaminated fuel, which increases the “solubility” of water in LPG [13]. This additive contains surfactants exhibiting the ability to solubilize water in the fuel. The affinity between water molecules and the surfactant increases with the decrease of temperature. This effect wholly protects physically bound water from crystallization in the temperatures below zero. The surfactants are dissolved in a mixture of low-boiling solvents of adequate partition coefficient between the phases of the system (Log P_{OW}). Repeated application of the additive leads to total removal of water present in the tank. The problem of valve freezing is solved this way, and the corrosion threat is removed or at least minimized.

This product has been used by the largest local LPG producers for years. A water solubilizing agent, called Aquagasol, and an anti-corrosion additive, Corimsol, besides good opinions from

the customers obtained a first grade award in the New Era Drive competition, in the category of innovative products.

Thanks to the application of Aquagasol additive, LPG contains water in concentration related to its production technology and operations in the distribution chain. The presence of water does not affect negatively the combustion process which is even improved.

4.1. Combustion of LPG with the addition of water

An interest in adding water to the combustion of hydrocarbon fuels has been observed since 1913. Hoptinson introduced atomized water to the combustion chamber of a compression-ignition engine which resulted in the reduction of detonative combustion [14].

Water to the combustion process can be supplied in three ways: as an additional stream independent from the fuel, with the air, or in the form of fuel-water emulsion. It was demonstrated that, from the three mentioned methods, the use of a fuel-water emulsion offers biggest advantages. The use of such emulsion causes more efficient reduction of soot particles than the introduction of water in air. Moreover, Cornet and Nero [15] demonstrated that the use of an emulsion notably influences the increase of fuel efficiency and decrease of the temperature of emitted exhaust gases. During studies on the combustion of water-fuel emulsions also, the decrease of nitrogen oxides emissions has been observed [16, 17].

Addition of water as a separate stream, in the form of emulsion or in the form of vapors, has been profoundly studied [18, 19, 20, 21, 22]. Studies carried out in order to reduce harmful components of exhaust gases indicate that the addition of water to the combustion process is a promising measure allowing reaching these results. It was demonstrated experimentally that the addition of water to the combustion process gives significant effects for the combustion process of liquid fuels. Harrington [18] has proven that the addition of water to the combustion process can suppress detonative combustion and reduce the emission of nitrogen oxides as an effect of reduction of combustion temperature. He also observed that the concentration of carbon (II) oxide did not change and the concentration of hydrocarbons increased slightly in the exhaust gases emitted to the atmosphere. Özcan and Söylemez [23] carried out a research work aimed at the evaluation of addition of water to the combustion process of LPG in a traditional, spark-ignited engine. In these studies, water was introduced to the suction collector. The results demonstrated that the addition of water to the suction manifold causes the cooling of air-fuel mixture, slows the combustion speed reducing the top combustion temperature, which, in turn results in the reduction by 35% of maximum NO_x emission, not changing CO and HC emissions. In Söylemez's and Özcan's work [24], the results of studies on the effect of water addition to the suction manifold on engine efficiency and the temperature of exhaust gases were presented. The results indicate that addition of water to suction manifold reduces the work of compression. Along with the increase of water-fuel weight ratio, the engine's torque, power, and thermal efficiency increased. Average increase of thermal efficiency for the water-fuel weight ratio of 0.5 was about 2.4% compared to the use of pure LPG for a tested range of an engine's rotational speeds. It was also found that along with the increase of the water-fuel ratio, the unitary fuel consumption and the temperature of exhaust gases decrease.

Addition of water to the combustion process of LPG causes the reduction of emission of harmful and toxic components of exhaust gases (NO_x, hydrocarbons, CO₂) and the reduction of fuel consumption.

An effect of water addition was studied in a spark-ignited engine fueled with liquefied gas on the temperature of exhaust gases and emission levels, for different fuel-air (F/A) ratios. The amount of formed nitrogen oxides (NO_x) depends on the fuel/air ratio, the maximum temperature, and combustion velocity. The results indicate that the maximum, 35% reduction of NO_x emission, is obtained by the introduction of water to the combustion of a lean mixture. The main cause of NO_x reduction is the decrease of temperature and the reduction of combustion velocity caused by the addition of water.

For a lean mixture, the concentration of carbon (II) oxide changes slightly with balanced fuel/air ratio, and increases dramatically when the fuel-air mixture becomes rich, surpassing the stoichiometric ratio. Water in the combustion process improves complete combustion by promoting carbon (II) oxide oxidation. The combustion of CO is slow and results in the delay in fuel combustion. Water vapor in the zone of hydrocarbon combustion seems to exhibit catalytic action in this process. In this way, supplying water to the combustion chamber causes the acceleration of the combustion process [25].

A research has been conducted [26] which was aimed at the evaluation of water addition to the process of LPG combustion in a spark-ignited engine on the emission of particular components of exhaust gases, fuel consumption, and the level of fogging of exhaust gases. In this work, liquefied gas was used whose composition was determined chromatographically (Agilent 6890N) (Table 2).

Component	% mol.	% wt.
Ethane	0.34	0.20
Propane	45.93	39.26
Propene	0.00	0.00
n-butane	52.77	59.47
Isobutane	0.77	0.87
Isobutene	0.19	0.21

Table 2. Composition of LPG fuel

In this work, the emission of exhaust gases during the New European Driving Cycle (NEDC) was tested. This cycle is presently confirmed in the regulations and commonly used test in the measurements of exhaust gas emissions for passenger cars and light utility vehicles in Europe [27]. Obligatory for all newly produced cars in Europe, the NEDC test consists of two parts: urban driving cycle, representing fully driving in the city (UDC), 4 times 195 s, and extra-urban driving cycle, lasting for 400 s [28].

For this study, a passenger car Daewoo Lanos, produced in 2000, equipped with a 16 valve, 1498 cm³ spark-ignited engine with an oxidation catalyst has been used.

The measurements of the emissions of exhaust gas components and fuel consumption were carried out in the Laboratory of Engines and Undercarriages, Automotive Industry Institute in Warsaw, equipped with a Schenck–Komeg EMDY chassis dynamometer with one roller of 48" diameter and MEXA 7200 exhaust gas analyzers produced by Horiba, including the following detectors:

- CO – AIA 7217 (NDIR method)
- CO₂ – AIA 7220 (NDIR method)
- O₂ – MPA 720
- HC – FIA 725 A (HFID method)
- NO_x – CLA 755A (chemiluminescence method)

as well as with a Opacimetr AVL 4390–G003 dynamometer.



Figure 7. Photography of a test stand (visible chassis engine test stand, air supply, water vapor supply, and exhaust gas analyzer)

The amount of fuel and water introduced into the combustion chamber was measured by the change of mass of gas cylinder and ultrasonic generator of water vapor located after the air filter, before the throttle. Water was introduced in the form of ultrasonically generated cold vapors.

The studies encompassed the following types of supplying the fuel to the engine:

- LPG
- LPG with the addition of 2.22% m/m of water (LPG + water vapor (dry steam)).

Emission

The results of hydrocarbon emissions in exhaust gases for the two types of fuel supply to the engine, that is, pure LPG and LPG with the addition of water vapor, are presented in Table 3.

	UDC	EUDC	NEDC
LPG	3.43	0.24	1.42
LPG + water vapor	2.88	0.23	1.21

Table 3. The results of measurement of hydrocarbon emissions (g/km)

In the mixed cycle, NEDC, similarly as in the case of UDC and EUDC, the emission of hydrocarbons is reduced as an effect of addition of water vapor to the combustion process in the engine.

The results of carbon and nitrogen oxides as well as particulate matter emission measurements are presented in Tables 4, 5, 6, and 7.

	UDC	EUDC	NEDC
LPG	10.86	1.34	4.86
LPG + water vapor	7.46	0.63	3.15

Table 4. Emission of CO, g/km

The data presented in Table 4 indicate that the lowest level of CO emission is observed in the EUDC cycle. The largest CO emission is observed in the urban drive cycle, in which the emission of CO for LPG is 10.86 g/km and is reduced by the addition of water vapor to 7.46 g/km. The emission in the mixed cycle resembles the trend characteristic for the urban driving cycle.

	UDC	EUDC	NEDC
LPG	206.81	107.93	144.46
LPG + water vapor	191.82	104.08	136.41

Table 5. Emission of carbon dioxide, g/km

Emission of carbon dioxide reaches the highest level (206.81 g/km) in the case of urban driving on pure LPG and is reduced by the addition of water vapor to 191.82 g/km. This is the highest drop among the tests carried out of CO₂ emission.

	UDC	EUDC	NEDC
LPG	0.12	0.18	0.16
LPG + water vapor	0.11	0.17	0.15

Table 6. Emission of nitrogen oxides, g/km

From the comparison of data presented in Table 6, it can be concluded that the maximum NO_x emission occurs in an extra-urban driving cycle, when the engine is supplied with pure LPG, reaching the value of 0.18 g/km. Addition of water vapor results in the reduction of NO_x emission by a few percent in each studied cycle.

For each cycle, after the addition of water vapor to the mixture supplying the engine, a significant drop in the emission of particulate matter is observed, depending on the type of test. The biggest reduction of particulate matter emission was noted for the extra-urban driving cycle (from 0.0081 g/km to 0.0034 g/km) (Table 7).

	UDC	EUDC	NEDC
LPG	0.0071	0.0081	0.0072
LPG + water vapor	0.0039	0.0034	0.0036

Table 7. Emission of particulate matter, g/km

Fuel consumption

Table 8 presents fuel consumption, depending on the type of driving cycle

	UDC	EUDC	NEDC
LPG	15.21	7.21	9.62
LPG + water vapor	13.81	6.88	8.92

Table 8. Fuel consumption, dm³/100 km

The analysis of this data allows the conclusion that addition of water vapor to the combustion process of LPG causes the reduction of fuel consumption. It is particularly visible in the urban driving cycle.

The analysis of the results of engine tests with the addition of water to the combustion in a spark-ignited engine fueled with autogas (LPG) confirms literature data, indicating that water

generally has good influence on the course of LPG combustion. Even a low concentration of water vapor in the fuel-air mixture causes significant reduction of toxic components in exhaust gases as well as reduction of fuel consumption. Particularly significant and important from the point of view of ecology is the reduction of particulate matter emission (Figure 8).

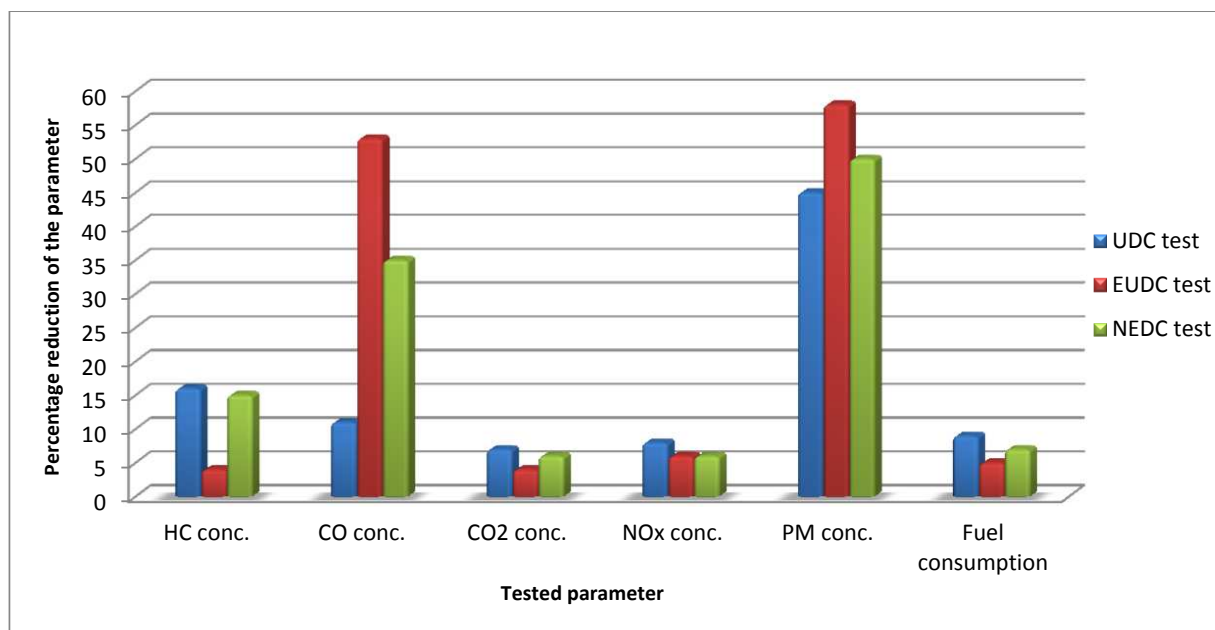


Figure 8. Percentage reduction of emission of exhaust gas components and fuel consumption depending on the type of test

The way of water addition to the LPG combustion process in a spark-ignited engine proposed in this work, turned out to be fully efficient and justifies further engine tests. Their aim will be the optimization and regulation of the amount of water added to the combustion of autogas as well as elaboration and construction of a water supply system.

5. Upgrading LPG as a motor fuel

A dominating way to use LPG as a motor fuel, at the present state of technology, is its controlled (sequential) dispensing into the suction manifold in gaseous state. This solution is rather complicated and not very rational. It requires liquid LPG to be evaporated by heating with cooling liquid, which requires starting of a cold engine on gasoline. Secondly, evaporated LPG cannot cool or cleanse the injector, which also leads to periodical dosing of gasoline to the engine fueled with autogas. Thirdly, such a form of LPG dispensing makes the use of additives more difficult, additives that could remove its disadvantages compared to gasoline.

A partial solution for the improvement of autogas quality, used in traditional fuel supply systems in spark-ignited engines, can be the use of a multifunctional additive [29]. The composition used in this invention significantly improves fuel lubricity and gives it adequate

cleaning properties. The additive should generally be used in 50 ppm m/m concentration, which requires very high purity of the base fuel (oil residue). It performs very well in the storage and distribution of LPG, providing most of all longer lifetime of pumps (lubricity) and cleanliness of pipelines, tankers, and fittings (cleaning properties). Fuel improved with such an additive is ideal for modern injection systems of liquid LPG into suction collectors or directly into the combustion chamber [30].

The given example indicates the need for further improvement of LPG quality in order to meet or even exceed modern gasolines in all aspects, including operating parameters.

The users of LPG-fueled cars notice the differences in the quality of a fuel related to its calorific value. Because of this they most often blame the owners of fuel stations and attribute them with bad will or lack of care toward customers. They exhibit in this way the lack of understanding of an important feature of this fuel, which is the dependence of density on the temperature and chemical composition.

6. Modeling of LPG density as a function of composition and temperature

The problem originates from dual types of measurements used in the LPG distribution chain – based on mass and volume. Producers, importers, and wholesalers use measurements based on mass while fuel stations are based on volume. The solution of this problem could be mass counters in the LPG distributors at the filling stations. Modern, precise mass counters are presently adapted for high mass flows and are used most often in fuel bases and wholesalers; however, the producers currently make also equipment adequate to count smaller amounts of this fuel [31].

At the intermediate stages of distribution, the algorithms for the conversion of mass units into the volume of the fuel and vice versa are used. Both in the law and internal regulations, there are no detailed descriptions of correlations between these quantities, connected with density. Because of both practical and scientific reasons, this problem was the subject of cooperative work between the leading producer of LPG in Poland – Orlen Gaz Ltd., a part of the PKN Orlen capital group – and the Institute of Chemistry, Branch of Warsaw University of Technology in Plock.

In the first stage of this study, the producer picked out 10 batches of LPG of highly varying hydrocarbon composition (Table 9).

The search for a mathematical model for LPG density as a function of hydrocarbon composition and temperature leads to the problem of determination of the functional dependency in a 7-dimensional space:

$$\rho = f(x_1, x_2, x_3, x_4, x_5, x_6, T)$$

This dependency can be searched for using, for example, interpolation or approximation.

Batch No.	Propane	Propene	Isobutane	n-butane	Butenes	Isopentanes	Empirical density
[-]	[%m/m] x_1	[%m/m] x_2	[%m/m] x_3	[%m/m] x_4	[%m/m] x_5	[%m/m] x_6	kg/dm ³ Q
1	38,8	9,2	25,8	21,6	3,9	0,5	0,5585
2	48,9	1,0	12,8	36,4	0,1	0,1	0,5590
3	47,4	2,6	18,5	29,4	1,2	0,2	0,5540
4	62,7	0,1	13,7	21,8	0,1	0,4	0,5455
5	48,0	4,3	11,7	26,4	8,9	0,2	0,5570
6	32,3	5,4	23,3	29,0	9,0	0,2	0,5640
7	33,0	3,6	20,5	28,6	12,9	0,4	0,5640
8	81,3	0,1	6,6	10,0	0,8	0,2	0,5320
9	83,8	0,5	4,9	6,9	3,2	0,1	0,5275
10	58,2	1,0	8,3	20,3	10,6	0,2	0,5510

Table 9. Hydrocarbon composition and density of LPG in 20°C (293,15K) [32]

After carrying out verifications of numerous mathematical models, a high susceptibility of numerical data (Table 9) to linear and exponential modeling has been noticed.

Assuming the following notifications:

T – temperature [K],

x_i – elementary composition of LPG fuel $\left[\frac{\text{kg}}{\text{dm}^3} \right]$,

w_i – determined weight coefficients [-],

b – determined shift coefficient [-].

Linear model assumes linear dependency of LPG density and chemical composition, which is described by the formula:

$$\rho = T \cdot x + b$$

where $x = w_1 \cdot x_1 + w_2 \cdot x_2 + w_3 \cdot x_3 + w_4 \cdot x_4 + w_5 \cdot x_5 + w_6 \cdot x_6$

$$\text{or } \rho = T \cdot \sum_{i=1}^6 w_i \cdot x_i + b$$

The exponential model is based on an exponential function and assumes exponential dependency of LPG density on the temperature and chemical composition, which is described by the formula:

$$\rho = T \cdot e^{-x} + b$$

Having the value of real (empirically measured) density Q for the hydrocarbon composition of a batch numbered k , the determination of predicted density, ρ , requires the determination of weight coefficients $w_1, w_2, w_3, w_4, w_5, w_6$, using the least squares method.

Assuming $\varepsilon = \sqrt{(\rho - Q)^2}$ as an error of obtained approximation, the minimum of ε has to be found.

For the linear model, in order to determine the weight coefficients $w_1, w_2, w_3, w_4, w_5, w_6$ and shift coefficient b , the minimization of the formula $\varepsilon = \sqrt{\left(T \cdot \sum_{i=1}^6 w_i \cdot x_i + b - Q\right)^2}$ has been carried out.

For the exponential model, the formula $\varepsilon = \sqrt{\left(T \cdot e^{-x} + b - Q\right)^2}$ was minimized, where $x = \sum_{i=1}^6 w_i \cdot x_i$.

Example of the results for the data presented in Table 9.

- For the linear model (for simplification $b=0$)

1,77E-05	1,81E-05	1,81E-05	2,14E-05	2,09E-05	8,56E-05
w_1	w_2	w_3	w_4	w_5	w_6

Table 10. Weight coefficients for linear model of LPG density and shift coefficient $b=0$

Projected density, for example, for the chemical composition number 4 is:
 $\rho = 293,15 \cdot (1,77 \cdot 62,7 + 1,81 \cdot 0,1 + 1,81 \cdot 13,7 + 2,14 \cdot 21,8 + 2,09 \cdot 0,1 + 8,56 \cdot 0,4) \cdot 10^{-5}$
 $\rho = 0,54578$

- For the exponential model

0,164081	-0,042763	0,126409	0,070149	0,190154	0,092549	0,555551
w_1	w_2	w_3	w_4	w_5	w_6	b

Table 11. Weight coefficients for exponential model of LPG density of composition 4

Projected density, for example, for the chemical composition number 4 using the exponential model is:

$$x = 0,164081 \cdot 62,7 - 0,042763 \cdot 0,1 + 0,126409 \cdot 13,7 + 0,070149 \cdot 21,8 + 0,190154 \cdot 0,1 + \\ + 0,092549 \cdot 0,4 = 13,60071131 \\ \rho = 293,15 \cdot e^{-13,60071131} + 0,555551 = 0,555914466$$

Batch number	Q	Linear model		Exponential model	
ρ	Q - ρ	ρ	Q - ρ		
1	0,5585	0,5556	0,0029	0,5584	0,0001
2	0,5590	0,5589	0,0001	0,5571	0,0019
3	0,5540	0,5561	-0,0021	0,5569	-0,0029
4	0,5455	0,5458	-0,0003	0,5559	-0,0104
5	0,5570	0,5563	0,0007	0,5564	0,0006
6	0,5640	0,5636	0,0004	0,5578	0,0062
7	0,5640	0,5687	-0,0047	0,5568	0,0072
8	0,5320	0,5296	0,0024	0,5556	-0,0236
9	0,5275	0,5279	-0,0004	0,5556	-0,0281
10	0,5510	0,5486	0,0024	0,5558	-0,0048

Table 12. Summary of empirical and projected densities for the data presented in Table 10, along with approximation errors

For the needs of work [33] an application was elaborated.

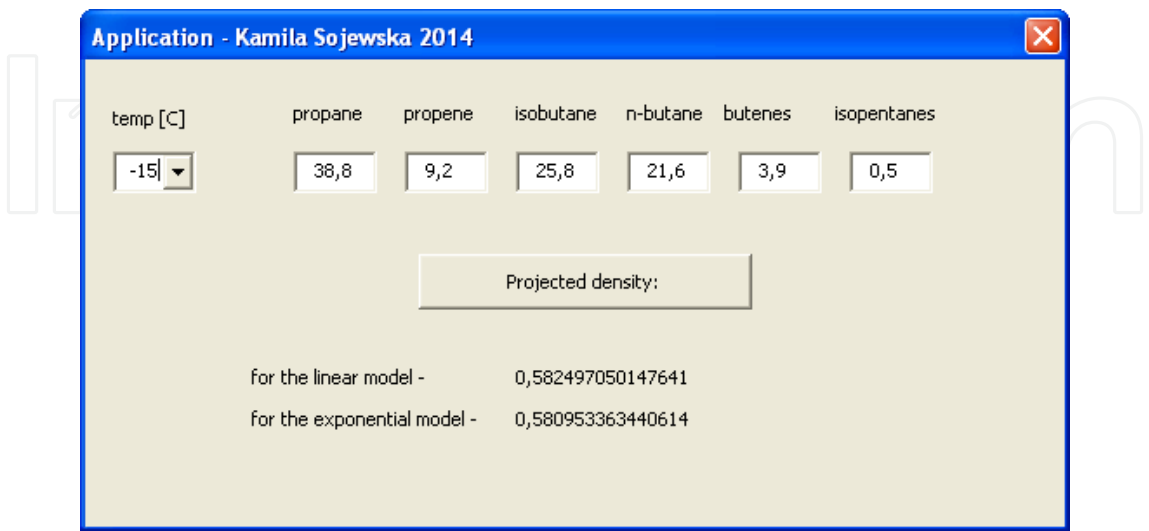


Figure 9. Application for the determination of LPG density basing on the chemical composition

Method of artificial neural networks

Using a thermodensimeter, the density of 10 LPG samples of different chemical compositions (Fig. 10) has been measured in the temperature range of -15°C to 20°C , every 1°C [32]. In this way, a set of experimental data was prepared containing 360 different values of LPG density $[\text{g}/\text{cm}^3]$.

Temp [°C]	Batch No	propane	propene	isobutane	n-butane	butenes	isopentan	Empirical density
-15	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5830
-14	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5815
-13	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5800
-12	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5800
-11	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5790
-10	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5785
-9	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5770
-8	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5755
-7	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5745
-6	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5725
-5	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5725
-4	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5700
-3	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5695
-2	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5685
-1	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5675
0	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5655
1	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5645
2	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5635
3	1	38,8	9,2	25,8	21,6	3,9	0,5	0,5625

Figure 10. Example of data set uploaded to the Statistica software

The data set prepared in this way was uploaded to the Statistica software and processed using artificial neural networks. The variable number 9, density, is treated as a starting value, a dependent variable. The other columns, describing the hydrocarbon composition of LPG, are treated as independent variables. In such an arrangement, the density of LPG is expressed as a value dependent on the temperature (in Kelvin or Celsius) and six variables describing the composition of the fuel.

As an effect of using Statistica Automated Neural Networks (SANN) procedure, three multilayer networks of the Multi-Layer Perceptron (MLP) type were obtained.

MLP network of 7-7-1 layer architecture turned out to be an optimal choice. Artificial neural network taught in this way becomes a support tool contributing to the projection of LPG density depending on hydrocarbon composition at a given temperature.

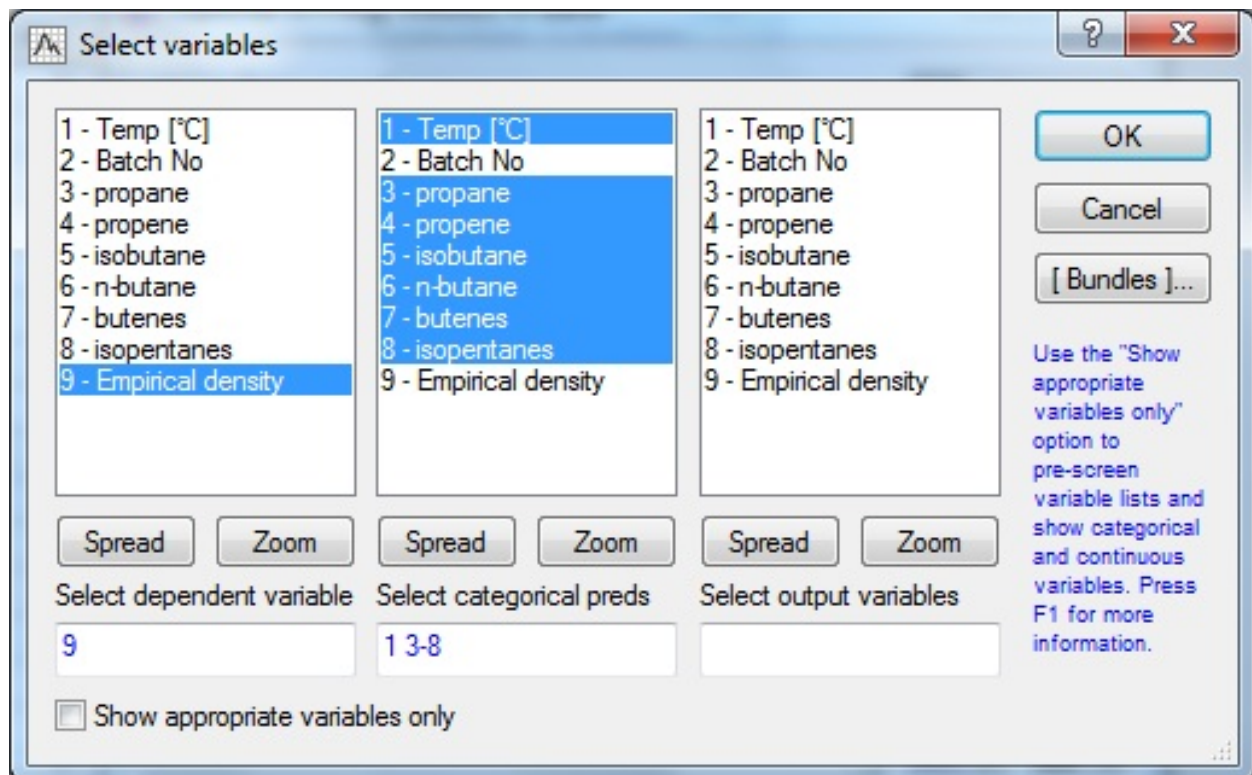


Figure 11. Interpretation of uploaded data

Empirical density Q	MLP 7-7-1 result ρ	Q - ρ
0,5830	0,5829	0,0001
0,5815	0,5818	-0,0003
0,5800	0,5807	-0,0007
0,5785	0,5775	0,0010
0,5770	0,5764	0,0006
0,5755	0,5753	0,0002
0,5745	0,5741	0,0004
0,5725	0,5719	0,0006
0,5790	0,5791	-0,0001
0,5780	0,5781	-0,0001
0,5765	0,5760	0,0005
0,5750	0,5750	0,0000
0,5740	0,5740	0,0000

Table 13. Comparison of densities, empirically determined and calculated by the neural network [34]

6.1. Analysis of a full spectrum of LPG hydrocarbon composition

An analysis seems justified of the influence of hydrocarbon composition on the LPG density in relation to the full spectrum of chemical compositions [35].

Batch number	Ethane	Propane	Propene	i-butane	n-butane	1-butene	i-butene	2-butene	i-pentane	Density in 15°C [kg/m³]
1	0,2	99,1	0,6	0,1	0,1	0,1	0,1	0,1	0,1	0,507
2	0,2	35,7	1,6	23,7	36,3	0,6	0,1	0,7	0,5	0,549
3	0,3	79,9	0,8	8,1	9,8	0,3	0,1	0,4	0,2	0,519
4	1,3	49,1	0,2	19,9	29,1	0,1	0,1	0,1	0,3	0,536
5	0,2	59,3	0,2	14,9	25,1	0,1	0,1	0,1	0,3	0,532
6	1,2	31,9	0,2	29,6	35,9	0,8	0,8	0,1	0,1	0,548
7	0,2	75,9	0,5	9,7	11,3	0,8	0,1	0,8	0,2	0,521
8	1	49,3	0,1	18,5	30,4	0,1	0,1	0,1	0,1	0,537
9	0,2	62,2	0,5	14,2	22,2	0,1	0,1	0,2	0,2	0,531
10	0,1	49,7	0,2	18,2	31,6	0,1	0,1	0,1	0,1	0,539

Table 14. Examples of extended chemical compositions of LPG

Specification of butene content in liquefied gas leads to the search for functional dependency in a 10-dimensional space (including temperature):

$$\rho = f(x_1, x_2, x_3, x_4, x_5, x_6, x_7, x_8, x_9, T)$$

The use of numerical methods, interpolation or approximation, described earlier seems to be proper and justified. However, in the case of processing a huge set of experimental data, which guarantees adequate accuracy, this method generates too complex and expanded numerical models.

6.2. Classification of LPG basing on the propane content

LPG distributed in the winter season contains about 60% propane. It is necessary in order to provide adequate vapor pressure in low temperature. During summer, very high vapor pressure can cause evaporation already in fuel lines, and that is why in the summer season LPG contains about 40% propane.

The proposed method of LPG classification based on its composition categorizes liquefied fuels into one of the three groups, depending on the propane content [36]:

- Group I: above 60%
- Group II: from 60% to 40%
- Group III: below 40%

The proposed method of LPG classification, depending on the percentage share of propane, which, in turn, has influence on the vapor pressure, imposes automatically the division of analyzed empirical data into three groups. It results in turn with a smaller number of samples being subject at the same time to numerical calculations. It is directly connected with lower complexity and simplification of numerical analysis. This simplifies in turn the search for mathematical models expressing LPG density as a function of hydrocarbon composition and temperature.

Group	Ethane	Propane	Propene	i-butane	n-butane	1-butene	i-butene	2-trans butene	i-pentane	Density [kg/dm ³]
I	0,2	99,1	0,6	0,1	0,1	0,1	0,1	0,1	0,1	0,507
	0,3	79,9	0,8	8,1	9,8	0,3	0,1	0,4	0,2	0,519
	0,2	75,9	0,5	9,7	11,3	0,8	0,1	0,8	0,2	0,521
	0,2	62,2	0,5	14,2	22,2	0,1	0,1	0,2	0,2	0,531
	0,2	71,3	0,4	15,9	0,1	0,1	0,1	0,1	0,1	0,524
	0,2	84,8	0,1	6	9	0,1	0,1	0,1	0,1	0,516
	0,6	60	9,2	21,2	6,6	0,4	0,6	0,7	0,2	0,525
	1,9	64	0,5	17,2	15,6	0,5	0,1	0,1	0,1	0,524
	0,4	61,7	8,8	12,5	14,7	0,8	0,1	0,5	0,2	0,526
	0,4	64	1,7	0,1	7,3	3,6	0,2	4,1	0,2	0,530
II	0,2	59,3	0,2	14,9	25,1	0,1	0,1	0,1	0,3	0,532
	1	49,3	0,1	18,5	30,4	0,1	0,1	0,1	0,1	0,537
	0,1	49,7	0,2	18,2	31,6	0,1	0,1	0,1	0,1	0,539
	1,1	41,3	0,3	25,2	27,9	3,4	0,6	0,1	0,1	0,542
	3,1	56,7	0,4	11,4	22,1	1,6	0,4	1,4	1,2	0,529
	3,5	56	0,2	13,8	25,3	0,1	0,1	0,1	0,7	0,527
	0,2	52,7	4,4	19,3	22,3	0,2	0,2	0,2	0,3	0,534
	1,5	58,1	0,2	16,8	21,7	0,1	0,1	0,1	0,7	0,530
	0,6	53,2	1,5	17,8	22,6	1,3	0,1	1,4	0,4	0,536
	0,8	49,7	11,4	24,2	10,2	0,8	0,7	1,1	0,2	0,531
III	0,2	35,7	1,6	23,7	36,3	0,6	0,1	0,7	0,5	0,549
	1	38,2	11,7	36,8	10,4	0,3	0,7	0,3	0,2	0,535
	0,4	32,4	10,8	42,9	10,4	0,4	1,3	0,7	0,1	0,542
	2,7	23,8	0,1	21,3	49,9	0,1	0,1	0,1	1,1	0,553
	2,6	23,3	0,1	21,2	50,1	0,2	0,1	0,1	1,1	0,554
	1	27,1	0,1	28,2	43,3	0,1	0,1	0,1	0,2	0,553
	1,1	36,8	1,4	35	10,7	12,4	2	0,1	0,1	0,545
	0,6	29,7	4,6	28,5	19,5	14,8	1,9	0,1	0,1	0,551
	0,8	33,5	1,7	10,9	36,7	0,1	0,1	9,2	0,2	0,555
	0,5	36,6	1,3	18,8	42,3	0,1	0,1	0,1	0,2	0,548

Table 15. Composition of the selected LPG samples, depending on the group, in the temperature of 15°C

Investigating the linear model of the dependency of density on the hydrocarbon composition and minimizing the error of approximated density given by the formula:

$$\varepsilon = \sum_{k=1}^{10} \left[Q_k - T \cdot \sum_{i=1}^9 w_i \cdot x_{ki} + b \right]^2$$

for each of three groups represented by 10 measurements, the values of weight coefficients, presented in Table 14, were obtained.

Weight coefficients										
w ₁	w ₂	w ₃	w ₄	w ₅	w ₆	w ₇	w ₈	w ₉	b	
Group I	4,30	1,84	3,08	2,95	1,02	-3,45	-7,80	4,58	-8,69	1,00
	E-05	E-05	E-05	E-05	E-05	E-04	E-04	E-04	E-04	E+00
Group II	2,26	1,66	1,62	1,66	1,46	1,10	6,66	2,39	4,09	1,00
	E-05	E-05	E-05	E-05	E-05	E-05	E-06	E-05	E-05	E+00
Group III	2,83 E-05	1,74 E-05	1,70 E-05	1,45 E-05	1,45 E-05	1,31 E-05	2,59 E-05	2,28 E-05	1,95 E-05	1,00 E+00

Table 16. Weight coefficients for the linear model

Approximate density values, determined for each out of 10 empirical values, are presented in Table 15.

Group								
I			II			III		
Density Q	Density ρ	Q - ρ	Density Q	Density ρ	Q - ρ	Density Q	Density ρ	Q - ρ
0,507	0,5094	-0,0024	0,532	0,5323	-0,0003	0,549	0,5497	-0,0007
0,519	0,5170	0,0020	0,537	0,5383	-0,0013	0,535	0,5355	-0,0005
0,521	0,5211	-0,0001	0,539	0,5382	0,0008	0,542	0,5415	0,0005
0,531	0,5329	-0,0019	0,542	0,5420	0,0000	0,553	0,5522	0,0008
0,524	0,5243	-0,0003	0,529	0,5294	-0,0004	0,554	0,5547	-0,0007
0,516	0,5133	0,0027	0,527	0,5263	0,0007	0,553	0,5532	-0,0002
0,525	0,5250	0,0000	0,534	0,5338	0,0002	0,545	0,5449	0,0001
0,524	0,5241	-0,0001	0,530	0,5300	0,0000	0,551	0,5511	-0,0001
0,526	0,5259	0,0001	0,536	0,5355	0,0005	0,555	0,5550	0,0000
0,530	0,5301	-0,0001	0,531	0,5311	-0,0001	0,548	0,5472	0,0008

Table 17. Comparison of empirically determined and approximated density values

In Table 15, similarly as in previous cases, Q represents empirical density and q approximated density. In order to summarize discussed methods of LPG density modeling on the basis of hydrocarbon composition at a given temperature, the differences between values of empirical density Q and approximated density q are presented in Table 16.

	Linear model	Exponential model	MLP 7-7-1	Classification of LPG basing on propane content (group I, II, III)		
		$ Q - q $		I	II	III
Min	0,00009	0,00009	0,00000	0,00000	0,00000	0,00000
Max	0,00469	0,02811	0,00100	0,00270	0,00130	0,00080
Median	0,00176	0,00550	0,00030	0,00020	0,00035	0,00050

Table 18. The comparison of the accuracy of discussed methods for predicting LPG density

7. Conclusions

In the past years, an increased interest has been observed in searching for such motor fuels, whose production and combustion results in lower emission of the main greenhouse gas, carbon dioxide. Because of environmental and economic considerations, the reduction of particulate matter, sulfur and nitrogen oxides emission, as well as the reduction of fuel consumption by vehicle engines are striven for.

From this point of view, a significant alternative for traditional motor fuels is fueling an engine with a liquefied mixture of propane and butane, called liquefied petroleum gas LPG or autogas. The advantages of liquefied hydrocarbon gases are particularly appreciated by the automotive industry.

On the background of increasing global LPG consumption, the achievements of Polish autogas industry in the area of production of automobile LPG systems, a number of bi-fuel vehicles, and logistical infrastructure were presented. The development of this industry is accompanied by research and implementation works, design and construction projects, as well as with promotion and marketing.

This fuel exhibits some disadvantages, the removal of which is a challenge to the autogas industry. The changes in the design of supply systems take place, and with regard to the fuel, quality improving additives are being tested, as well as addition of water to the LPG combustion process.

Successful solving of the problems indicated in this chapter will be a huge step forward to the improvement of competitiveness of LPG as a motor fuel.

In this chapter, several threads of innovative actions are presented, directed at further improvement of logistics efficiency, more complete utilization of advantages of LPG as a motor

fuel, and indirectly the consolidation of a positive image of autogas as a fuel environmentally friendly.

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